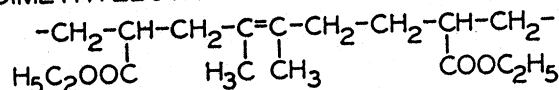


# Preparation and Vulcanization of Unsaturated Acrylic Elastomers—I

W. C. Mast<sup>1</sup> and C. H. Fisher<sup>1</sup>

IT WAS shown in earlier papers (1, 2)<sup>2</sup> from this Laboratory that methyl and ethyl acrylate resemble isobutylene (2) in that they can be copolymerized with a small proportion of a polyolefinic monomer, such as butadiene or isoprene, to vulcanizable copolymers. Rubber-like vulcanizates were obtained (1, 2) by compounding the copolymers—assumed to contain olefinic unsaturation—with sulfur and accelerators and molding the compounded stock at approximately 150° C. This finding was followed by an expansion of the acrylic elastomer investigation to include (a) the preparation and vulcanization of additional unsaturated acrylic elastomers, (b) the development of special recipes (4) capable of curing ethyl polyacrylate and similar saturated acrylic resins, and (c) a search for functional groups other than olefinic linkages that can be used conveniently for vulcanization purposes.<sup>3</sup>

## DIMETHYLBUTADIENE COPOLYMER



## CROTYL ACRYLATE COPOLYMER

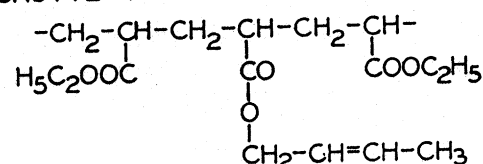


Fig. 1. Dimethylbutadiene and Crotyl Acrylate Copolymers

This paper reports the vulcanization of additional unsaturated acrylic elastomers prepared by copolymerizing acrylic esters with a small proportion of 11 dienes, 11 polyolefinic esters, and six ethers (Table 1). The purpose of the work was to prepare improved elastomers, ascertain qualitatively the tendency of the polyolefinic monomers of widely different character to form cross-linked copolymers, and to obtain information on the effect of polymer structure (as determined by the selection of monomers) on the rate of curing and properties of the vulcanizates.

It would be expected that the unsaturated copolymers<sup>4</sup> obtained with the polyfunctional monomers of Table 1 would differ considerably in structure, leading to differences in curing rate and properties of the vulcanizates. These differences could arise from dissimilarities in both the structure and location of the olefinic linkages. For example, the unsaturation in the 2,3-dimethylbutadiene copolymers should be principally in the polymer chain and characterized by the presence of two methyl groups; whereas the unsaturation in the crotyl acrylate copolymers should be principally in side chains and subject to less steric hindrance. (See Figure 1.)

## Experimental Details

The polyolefinic monomers (Table 1) were prepared here (2) or obtained from other organizations. When desirable and feasible, the monomers were further purified by washing with alkali and distillation.

The monomers were emulsion polymerized by the method previously described (16). The polymerizations were carried out in a round-bottom, three-neck Pyrex flask fitted with glass-ground joints for a condenser, water-sealed glass stirrer, and thermometer well. Water and emulsifier were stirred and heated (below 85° C.) in the flask until a smooth dispersion or solution was obtained. The monomers were then added, and polymerization was induced by heat and catalysts (Table 2).<sup>5</sup> Ammonium persulfate was used to initiate polymerization in most instances, but hydrogen peroxide, benzoyl peroxide, and succinic acid peroxide were also used. Acrylonitrile and dodecyl mercaptan were used in some polymerizations to decrease cross-linkage. The emul-

TABLE 1  
POLYENES USED IN THE PREPARATION OF ACRYLIC ESTER COPOLYMERS\*

Polyene	Boiling Point, °C.	Percentage Equivalent to 2% Butadiene†
Butadiene-1, 3.....	-57 <sup>13</sup>	2.00
Isoprene.....	33.5	2.52
Pentadiene-1, 3‡.....	42-44	2.52
Cyclopentadiene.....	41-42	2.52
2, 3 Dimethylbutadiene-1, 3§.....	71	3.04
Myrcene  .....	68 <sup>23</sup>	2.52
Divinyl benzene.....	71	4.84
Allo-oimene**.....	90 <sup>21</sup>	2.52
2-Methylpentadiene-1, 3.....	76	3.04
Chloroprene.....	59.4	3.27
Vinyl cyclohexene-3.....	Not distilled	4.00

POLYOLEFINIC ESTERS USED IN THE PREPARATION OF ACRYLIC ESTER COPOLYMERS

Ester	Boiling Point, °C.	Percentage Equivalent to 2% Butadiene†
Allyl maleate.....	78 <sup>15</sup>	3.67
Furfuryl acrylate††.....	93 <sup>16</sup>	2.83
Crotyl acrylate††.....	60 <sup>23</sup>	4.70
Cinnamyl acrylate††.....	108 <sup>17</sup>	7.0
Citronellyl acrylate††.....	108 <sup>18</sup>	7.8
Geranyl acrylate††.....	116 <sup>19</sup>	3.87
Allyl lactate.....	Not distilled	6.3
Allyl diglycol carbonate.....	160 <sup>20</sup>	10.1
Rhodanyl acrylate††.....	107 <sup>22</sup>	7.8
4-Methyl-4-penten-2-yl acrylate††.....	62 <sup>24</sup>	5.7
Allyl phthalate.....	150 <sup>1</sup>	...

POLYOLEFINIC ETHERS USED IN THE PREPARATION OF ACRYLIC ESTER COPOLYMERS

Ether	Boiling Point, °C.	Percentage Equivalent to 2% Butadiene†
Vinyl ether.....	39	2.6
Di-allyl glycol.....	35 <sup>1</sup>	5.26
Allyl ether.....	94.3	3.62
Methallyl ether.....	...	4.65
Tetra-allyl-alpha-methyl-glucoside††.....	160 <sup>15</sup>	4.36
Allyl starch§§.....	...	10

\*The sources of these monomers are acknowledged at the end of the paper.

†Proportion in % of the polyolefinic monomer required to give a copolymer having the calculated vulcanizable unsaturation of a 98% ethyl acrylate-2% butadiene copolymer (assuming one residual double bond).

‡Prepared in the Northern Regional Research Laboratory by pyrolysis of the corresponding glycol diacetate (10).

§One of the samples used was prepared by pyrolysis of pinacol diacetate (11). Myrcene: (CH<sub>3</sub>)<sub>2</sub>C=CHCH<sub>2</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>.

||Purified by fractional recrystallization.

\*\*Allo-oimene: (CH<sub>3</sub>)<sub>2</sub>C=CHCH<sub>2</sub>CHC(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>.

††Preparation described in (12).

‡‡Preparation described in (13).

§§Preparation described in (14).

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<sup>2</sup> Numbers in parentheses refer to Bibliography items at end of this article.

<sup>3</sup> The vulcanization of saturated acrylic elastomers containing halogen, nitro, cyanoethyl and other groups with sulfur and accelerators has been the subject of several papers (4-9). The vulcanization of an ethyl acrylate-methyl vinyl ketone copolymer with sulfur and accelerators, demonstrating the usefulness of the methyl ketone group in vulcanization, will be described in a forthcoming paper.

<sup>4</sup> Throughout this paper the term "copolymer," used in the broader sense (15), includes any product made by polymerizing a mixture of monomers. Possibly amenability to vulcanization with sulfur and accelerators indicates that true copolymers were formed.

<sup>5</sup> The mention of specific brands in Table 2 and in other parts of the paper should not be construed as an endorsement or recommendation of these brands over others not tested.

TABLE 2. EMULSION POLYMERIZATION OF DIENE-ETHYL ACRYLATE MIXTURES

Expt. No.	Diene	%			Ammonium Persulfate	Tergitol Penetrant #4*	Solids	Temperature °C.	Time, Hours	Yield %
		Acrylonitrile	Dodecyl Mercaptan							
E31†	Butadiene	2	6	..	0.10	1	25	75-77	5.0	50
E32†	Butadiene	2	6	..	0.15	1	25	75-77	5.0	60
E33†	Butadiene	2	6	..	0.22	1	25	75-77	5.0	70
D45	Isoprene	2.1	..	..	0.13	0.75	25	77-92	0.8	95.5
D46	Isoprene	2.1	6	..	0.09	0.75	25	77-92	1.7	91
D47	Isoprene	2.1	6	0.10	0.09	0.75	25	77-92	1.5	92
D48	Isoprene	4.2	6	0.10	0.10	0.75	25	75-92	1.7	77
D49	Isoprene	8.4	6	0.10	0.14	0.75	25	75-92	2.3	85
D97	Isoprene	2.1	6	..	0.11	0.75	37.5	77-92	3.5	95
D125	Isoprene	2.1	6	....	0.09	0.75	37.5	77-92	7.0	87
D50	Piperylene	2.1	..	..	0.10	0.75	25	78-92	2.2	97
D51	Piperylene	2.1	6	..	0.06	0.75	25	78-92	1.3	91
D52	Piperylene	2.1	6	0.10	0.08	0.75	25	78-92	1.2	94
D53	Piperylene	4.2	6	0.10	0.09	0.75	25	78-92	1.7	91
D81	Piperylene	2.1	6	..	0.08	0.75	25	78-92	2.7	86
D82	Piperylene	2.1	9.3	..	0.075	0.75	25	78-92	5.7	77
D83	Piperylene	2.1	6	..	0.05	0.75	25	78-92	2.5	87.5
E18	2, 3 Dimethylbutadiene	2.6	0	..	0.07	1.75	20	77-92	0.7	93
E19	2, 3 Dimethylbutadiene	2.6	6	..	0.05	1.75	20	77-92	1.0	90

\* Moisture free basis.

† In agitated sealed bottles under pressure.

sions were refluxed during the polymerization, and at refluxing temperature a period of 30 minutes to several hours was usually required. The temperature rose during the polymerization from about 72 to 82° C. and from 82 to 92° C. when methyl acrylate and ethyl acrylate, respectively, were the principal monomers. Hence the course of the polymerization could be followed roughly by noting the temperature. The extent of polymerization could be followed also by observing changes in the refractive index, density, and solids content of the emulsion. At the end of the polymerization any unchanged methyl acrylate or ethyl acrylate was removed by blowing steam through the emulsion.

The refluxing temperature was lowered at the beginning of the polymerization when low-boiling dienes were used (butadiene copolymers were prepared in pressure vessels). Gentle refluxing was maintained, and the temperature was allowed to rise gradually during the polymerization. In some instances preliminary runs were required to determine the correct amount of catalyst. The minimum amount of catalyst that would cause polymerization within a reasonable time (usually one hour to three hours) was used. It was found desirable to have little or no induction period before the start of the polymerization to reduce the possibility of side reactions of the monomers or emulsifying agents and to prevent excessive precoagulation during the reaction. The monomers were mixed immediately before being added to the aqueous phase or added separately. The addition of sufficient catalyst in one lot to cause polymerization was preferable to several additions of smaller quantities at half-hour or longer intervals because the total required quantity of catalyst was less, and side reactions were less troublesome. A period of five to 15 minutes was usually required to heat the mixture to refluxing, and the induction period could often be reduced or virtually eliminated by adding the catalyst just before heating was started.

When polymerization was considered complete, the latex was coagulated by adding it while hot to twice its volume of hot, rapidly stirred, 5% sodium chloride solution. The resulting fine, discrete, rubber-like crumb was washed five to seven times with hot distilled water. (Washing was continued until the wash water gave a slight or negative test for chloride ion.) No trouble was encountered when the temperature of the wash water was kept above 90° C., but the polymer lumped together and was difficult to wash at lower temperatures. The copolymers were air dried for several days at room temperature. Randomly chosen samples dried in this manner contained less than 0.5% water.

The solubility characteristics of the copolymers were ascertained, and toluene solutions of the soluble copolymers were prepared and used in the determination of intrinsic viscosity. Insolubility was generally considered evidence of cross-linkage, effected either through the olefinic unsaturation or caused by free radical cross-linkage (initiated by the polymerization catalyst) of the ethyl polyacrylate portion of the copolymer chain.<sup>6</sup> Most of the insoluble copolymers formed loose, easily dispersed gels that were entirely different from the gel fraction of GR-S rubber and probably were indicative of a low degree of cross-linkage. The soluble and insoluble fractions of the copolymers were not examined in detail, although a study of the type of gel and the ease of its dispersion might have given significant results.

The copolymers were judged further by their general appearance, the ease with which they could be drawn (manually) into filaments, their behavior on milling, and the physical properties of the vulcanizates. A small rubber mill<sup>7</sup> was used for the compounding (80 to 110° F.). The stocks were cured as slabs 0.03-inch thick and tested on a modified Scott L-6 tester. Brittle points were determined by the method of Selker, Winspear, and Kemp (22). The work reported herein was done prior to the discovery in 1945 (6) that milling at about 160° F. is preferable to milling at lower temperatures.

### Ethyl Acrylate-Diene Copolymers

Preparation of the diene copolymers of Table 2 required substantially larger amounts of catalyst than that normally used to polymerize ethyl acrylate.<sup>8</sup> Possibly the retarding effect of the diene and the use of increased amounts of catalyst were partly responsible for the fact that the diene copolymers were different from ethyl polyacrylate in being insoluble in toluene, having a drier appearance and less tack, and in being less easily drawn into filaments. The diene copolymers resembled other ethyl acrylate polymers and copolymers prepared in this Laboratory in that their behavior on being drawn with the fingers into filaments was related to their general appearance and their solubility characteristics. For example

<sup>6</sup> Ethyl polyacrylate made in the presence of relatively large amounts of polymerization catalyst is insoluble and presumably cross-linked (17). Benzoyl peroxide has been used to cross-link ethyl polyacrylate (4) and other polyesters (18, 19). Presumably the cross-linkage is caused by decomposition of the benzoyl peroxide into free radicals, removal of hydrogen from the polymer chain to yield a polymer free radical, and combination or union of two of the polymer free radicals. A more detailed explanation will be found in (4) and (19). The scale of operation was somewhat larger than that used by Fryling (20) and Garvey (21) in preparing and testing small quantities of elastomers.

Ethyl acrylate of moderate purity can be readily emulsion polymerized (refluxing) with 0.005% or less of ammonium persulfate in one hour; the temperature of the vapor increases from 82 to 92° C. Monomer mixtures containing 5% 2-chloroethyl vinyl ether or 2-chloroethyl acrylate (4, 17) can be polymerized under similar conditions without appreciably increasing the catalyst concentration.

the polymers that could be readily drawn (slowly to allow for cold flow) into threads and eventually into virtually invisible filaments were usually soluble in benzene, toluene, ethyl acetate, dioxane, and similar solvents. The polymers that gave coarse threads having uneven sections usually formed dispersible gels with solvents. Polymers that tore across thick sections and contained lumpy portions in the stretched area yielded less dispersible gels or remained as discrete swollen masses.<sup>9</sup>

Butadiene, isoprene, and dimethylbutadiene had diminishing tendencies to form cross-linked copolymers during polymerization in the order named. Isoprene and piperylene had about the same tendency to form cross-linked copolymers. The best vulcanizates were obtained from the isoprene, piperylene, or dimethylbutadiene copolymers. The vulcanizates from the diene copolymers appeared less lively, that is, retracted more slowly, than the vulcanizates from the ethyl acrylate-chloropropyl acrylate and chloroethyl vinyl ether copolymers (4, 7).

TABLE 3. VULCANIZATION\* OF DIENE-ETHYL ACRYLATE COPOLYMERS  
(Preparation Described in Table 2)

Copolymer No.	Curing Time at 298° F. Min.	Tensile Strength P.S.I.	Ultimate Elongation %	Shore A Hardness	Brittle Point °C.
E31 Butadiene	180	1280	270	61	..
E32 Butadiene	120	1240	290	60	..
E33 Butadiene	120	1160	280	62	..
D45 Isoprene	120	630	730	49	-15
D46 Isoprene	120	1130	680	55	-11
D47 Isoprene	120	990	750	58	-9
D48 Isoprene	120	1200	370	66	-7
D49 Isoprene	60	1190	210	65	-4
D47 Isoprene	180	1190	550	60	-10
D125 Isoprene	180	840	560	54	..
D50 Piperylene	60	820	780	48	-18
D51 Piperylene	180	1110	910	58	-8
D52 Piperylene	120	510	1020	60	-8
D53 Piperylene	60	670	640	62	-8
D81 Piperylene	120	1020	590	62	-6
D82 Piperylene	60	920	770	55	-4
D83 Piperylene	60	940	830	50	..
E18 2, 3 Dimethylbutadiene	240	930	530	53	..
E19 2, 3 Dimethylbutadiene	240	1310	450	62	..

\*Recipe: copolymer, 100 parts; 2-mercapto benzothiazole, 0.5 part; zinc oxide, 5 parts; stearic acid, 2 parts; sulfur, 2 parts; tetramethyl thuram disulfide, one part; and SRF carbon black, 30 parts.

<sup>9</sup> These observations are based on the dissolution or dispersion of approximately 0.1 g. of polymer in 100 ml. of toluene.

Earlier results, obtained in a study of ethyl acrylate-allyl maleate copolymers, showed that dodecyl mercaptan and acrylonitrile were helpful in decreasing cross-linkage. In the present study neither mercaptan nor acrylonitrile was noticeably beneficial in attempts to prepare soluble diene copolymers.

The vulcanizates obtained from the butadiene copolymers had tensile strengths of 1100 to 1300 p.s.i., but the ultimate elongation was slightly under 300% (Table 3).

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(To be concluded)

# Preparation and Vulcanization of Unsaturated Acrylic Elastomers—II

W. C. Mast<sup>1</sup> and C. H. Fisher<sup>1</sup>

**I**SOPRENE COPOLYMERS. Most of the isoprene vulcanizates had slightly lower tensile strengths, but much higher elongations than the butadiene vulcanizates (Table 3).<sup>2</sup> This fact and the higher boiling point of isoprene made this diene appear more attractive than butadiene as a copolymerizing monomer.

Isoprene copolymers were vulcanized successfully with (a) sulfur with various accelerators, (b) quinone dioxime and red lead, (c) benzoyl peroxide with various reinforcing agents, and (d) sulfur with litharge (Table 4). The results show that a variety of curing<sup>3</sup> and reinforcing agents can be used to produce different types of vulcanizate. Harder and stronger vulcanizates were obtained by using larger proportions of Furnex beads or a harder black (Micronex). Both zinc oxide and calcium carbonate (Kalvan) were employed satisfactorily as reinforcing agents in the absence of carbon black.

The isoprene-ethyl acrylate copolymer was blended with both Butyl rubber (3)<sup>4</sup> and Paraplex X100 (18), and the blends were satisfactorily vulcanized, both with

sulfur and accelerators and with benzoyl peroxide (Table 5). The vulcanizates containing either butyl rubber or Paraplex X100 (rubbery polyester) had lower brittle points than the vulcanizates made entirely from the isoprene copolymer.

The general effect of using methyl acrylate instead of the ethyl ester in preparing the isoprene copolymers was to increase the tensile strength, hardness, and brittle point (Table 6). The vulcanizate from the copolymer made of 92% methyl acrylate, 6% acrylonitrile, and 2% isoprene had a tensile strength and elongation of 1720 p.s.i. and 500%, respectively. The use of allyl maleate instead of methyl acrylate, which required more catalyst in the preparation of the copolymer, seemed detrimental (Table 6, Expt. D117).

**PIPERYLINE COPOLYMERS.** The piperylene copolymers were somewhat like the isoprene copolymers in that their vulcanizates had relatively high tensile strengths and elongations. The effect of increasing the amount of carbon black was to increase the tensile strength and hardness and decrease the elongation (Table 7).

TABLE 4. VULCANIZATION OF ISOPRENE-ETHYL ACRYLATE COPOLYMER WITH VARIOUS RECIPES\*

Expt. No.	Parts per 100 Parts of Copolymer										Curing Time at 298° F. Min.	Tensile Strength P.S.I.	Ultimate Elongation %	Shore A Hardness	Brittle Point °C.
	Captax	Zinc Oxide	Stearic Acid	Sulfur	Furnex Beads	Micronex Beads	Tuads	Red Lead	Quinone Dioxime	Other Agents					
933	0	5	3	0	60	0	0	10	2		180	2160	140	86	—10
934	0.5	5	2	2	30	0	1	0	0		180	1190	550	60	
937	0.5	5	2	2	0	30	1	0	0	0.35, Rodo 0	120	1230	420	71	
938	0.5	5	2	2	0	30	1	0	0	0.35, Rodo 10	60	1270	480	68	—8
939	0.5	5	2	2	0	30	1	0	0	0.35, Rodo 0; 0.35, Rodo 10	20†	1160	500	68	
940	0	0	0	0	0	0	0	0	0	150 Iron oxide; 5 Luperco A	240	1120	490	57	
953	0.5	5	2	2	30	0	0	0	0	1, Butesac	120	1060	570	60	—10
954	0.5	5	2	2	20	0	1	0	0	20, Kalvan	20†	250	870	45	
987	0	0	0	0	0	0	0	0	0	100, Iron oxide; 5 Luperco A	240	1230	320	82	
988	0.5	50	2	2	0	0	1	0	0		180	1000	760	54	—9
989	0.5	5	2	2	0	0	1	0	0	40, Kalvan	120	830	610	51	
1037	0.5	5	2	2	30	0	0	0	0	2, Santocure	180	940	670	55	
1038	0.5	5	2	3	30	0	0	0	0	2, R-2 crystals	180	1160	520	50	—7
1039	0.5	5	3	1.5	30	0	0.75	0	0	0.75, Selenac	90	810	530	49	
1040	0	5	2	1.5	30	0	1	0.5	0	1.5 Selenac	120	590	880	35	
1041	0	0	0	2	30	0	0	0	0	5, Litharge	180	1090	540	52	—7
1046	0	5	2	2	30	0	1	0	0	0.5, Rotax	180	840	560	54	
1043	0.5	5	2	2	30	0	1	0	0		10	220	860	39	
1053	0	0	0	0	0	0	0	0	0	5, Luperco A; 125, Rayox	40	180	610	44	
1054	0	0	0	0	0	0	0	0	0	5, Luperco A; 125, Raycal					

\*Copolymer used in the 900 series experiments was prepared in Experiment D97, Table 2; that used in the 1000 series experiments was prepared in Experiment D125, Table 2.  
†At 210° F.

TABLE 5. BLENDS OF ISOPRENE-ETHYL ACRYLATE COPOLYMER WITH BUTYL RUBBER\* OR PARAPLEX X100†

Expt. No.	% by Weight			Parts per 100 Parts		Cure		Tensile Strength, Lb. Sq. In.	Ultimate Elongation, %	Shore A Hardness	Brittle Point °C.	Tensile Product
	Isoprene Copolymer	Butyl Rubber A	Paraplex X100	Zinc Oxide	Sulfur	Temp. °F.	Min.					
934†	100	0	0	5	2	298	180	1190	550	60	—10	655
950†	80	20	0	4	1.6	298	120	1060	580	55	—11	615
951†	50	50	0	2.5	1	298	120	1040	600	55	—40	625
952†	20	80	0	1	0.4	298	120	1840	730	53	—57	1340
1027†	0	100	0	0	0	298	180	2340	790	41	—65	1850
1030§	100	0	0	0	0	260	10	850	330	53	—7	280
1031§	90	0	10	0	0	260	10	880	400	58	—10	350
1032§	80	0	20	0	0	260	20	740	470	55	—17	350
1033§	65	0	35	0	0	260	20	950	420	54	—28	400
1034§	40	0	60	0	0	260	40	1170	420	60	—36	490
1035§	0	0	100	0	0	260	40	1570	370	62	—45	580

\*Butyl Rubber A contained 5 parts zinc oxide and 1.5 part sulfur; other ingredients were 0.5-part Captax, 2 parts stearic acid, 30 parts Micronex beads, and 1 part Tuads.

†Blend (100 parts) compounded with 4.5 parts Luperco A and 80 parts Kalvan; Paraplex X100 is a polyester obtained from the Resinous Products & Chemical Co., Philadelphia.

‡Isoprene copolymer prepared in Experiment D97, Table 2.

§Isoprene copolymer prepared in Experiment D125, Table 2.

D56, Table 13, gave a vulcanizate that was superior in combined tensile strength and ultimate elongation (1280 p.s.i. and 960%) to any of the other vulcanizates obtained in the present study. The vinyl ether copolymers made in two subsequent experiments gave pitted vulcanizates. It has been shown that vinyl ether has little tendency to form cross-linked copolymers (26). Nozaki (27) has published information on the copolymerization of vinyl ether.

An ethyl acrylate-allyl starch (14) copolymer, which appeared to be cross-linked, could not be compounded. The ethyl acrylate-allyl ether product was extremely soft and tacky, and its vulcanizates were badly pitted. The methallyl ether product (presumably of low molecular weight and plasticized with methallyl ether) also was unusually soft and sticky. The diallyl ether of ethylene glycol (13) seemed much more suitable for making vulcanizable acrylic resins than either allyl ether or methallyl ether (Table 13).

### Summary and Conclusions

Ethyl acrylate was copolymerized with small proportions of 11 dienes, 11 polyolefinic esters, and six polyolefinic ethers in an attempt to prepare olefin-containing acrylic elastomers that would vulcanize readily, yielding products having improved rubbery characteristics. In general, the resulting copolymers were insoluble in organic solvents, presumably because of cross-linkage. Acrylonitrile and dodecyl mercaptan appeared beneficial in the copolymerization of ethyl acrylate with polyolefinic esters, but of questionable value in the diene polymerizations.

The best vulcanizates from the standpoint of tensile strength and elongation were obtained from an ethyl acrylate-acrylonitrile-vinyl ether copolymer. Some preparations of this copolymer, however, had a tendency to pit and bubble during vulcanization.

Isoprene, piperylene, and 2,3-dimethylbutadiene were more suitable for preparing vulcanizable ethyl acrylate copolymers than the other dienes studied; their vul-

canizates had moderately high tensile strengths and elongations. Some of the dimethylbutadiene-ethyl acrylate copolymers were soluble.

Crotyl acrylate and geranyl acrylate, when copolymerized with ethyl acrylate, yielded copolymers that gave vulcanizates having moderately high tensile strengths and elongations ranging from 300 to 400%.

The physical properties of the vulcanizates prepared from unsaturated acrylic copolymers were not superior to those of the chloropropyl acrylate and chloroethyl vinyl ether products described previously (4, 7).

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C. E. Rehberg and Marion B. Dixon prepared the alkenyl acrylates (12) and some of the other polyolefinic esters, including the maleate of allyl lactate (28).

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TABLE 6. EFFECT OF METHYL ACRYLATE ON THE PROPERTIES OF ISOPRENE-ACRYLIC ESTER VULCANIZATES\*

Expt. No.	% Ethyl Acrylate    Methyl Acrylate    Ammonium Persulfate			Temp. °C.	Time, Hours	Yield, %	Curing Time at 298° F. Min.	Tensile Strength P.S.I.	Ultimate Elongation %	Shore A Hardness	Brittle Point °C.
D97	92	0	0.11	74-90	2.7	95	180	1190	550	60	....
D106	83	9	0.18	75-92	3.5	92	240	890	960	57	-10
D107	76	16	0.11	75-91	2.5	90	180	1290	680	61	-8
D108	0	92	0.24	70-89	4.7	91.5	240	1720	500	96	14
D109	62	30	0.16	75-92	4.0	90	180	1310	560	62	0
D110	40	52	0.27	72-75	3.5	97.5	...	...	...	...	...
D117†	89	0	0.41	76-92	4.0	92	120	1040	290	55	....

\*Monomer mixtures also contained 2% isoprene and 6% acrylonitrile; samples were prepared as 40% emulsions with 0.75% Tergitol Penetrant # 4 as emulsifying agent. Copolymers compounded as in Table 3.

†Monomer mixture contained 3% allyl maleate.

TABLE 7. VULCANIZATION OF PIPERYLENE-ETHYL ACRYLATE COPOLYMER WITH VARIOUS RECIPES\*

Expt. No.	Parts per 100 Parts of Copolymer								Tensile Strength, P.S.I.	Ultimate Elongation %	Shore A Hardness
	Captax	Stearic Acid	Sulfur	Red Lead	Quinone Dioxime	Furnex Beads	Tuads	Zinc Oxide			
893	0.5	2	2	0	0	30	1	5	1020	590	62
894	0	3	0	10	2	60	0	5	1460	310	83
899	0	3	0	10	2	30	0	5	910	420	57
900	0	3	0	10	2	45	0	5	1340	380	73

\*The piperylene copolymer was prepared in Experiment D81, Table 2; samples were cured for two hours at 298° F.

TABLE 8. COPOLYMERS OF 2,3-DIMETHYLBUTADIENE-1,3 AND ETHYL ACRYLATE\*

Expt. No.	2,3-Dimethylbutadiene 1,3 %	Acrylonitrile %	Ammonium Persulfate % of Monomer	Time, Hours	Yield, %	Intrinsic Viscosity of Copolymer†	Curing Time at 298° F. Hours	Tensile Strength P.S.I.	Ultimate Elongation %	Shore A Hardness
E110	2.6	6	0.043	1.0	96	1.38	2	1340	590	65
E111	5.2	6	0.060	2.0	94	1.10	2	1080	520	70
E135†	4.6	..	..	3.3	75	..	2	350	430	63
E136	4.6	..	0.015	1.0	95	..	3	1140	310	62
E137	10.0	..	0.012	2.5	90	..	3	1340	180	68
E138	15.0	..	0.019	2.2	70	..	1	1190	260	68
E159	5.0	..	0.010	3.5	94	1.97	2	1020	310	60
E160	2.0	..	0.012	4.0	81	2.49	2	1080	580	55
E161	10.0	5	0.048	5.5	94	1.22	2	1120	230	62
E162	10.0	..	0.025	3.5	100	Insol.	2	960	200	62
E163	2.0	5	0.028	3.0	99	2.70	2	1320	460	56
E164	5.0	5	0.025	3.0	92	1.73	2	1160	390	63
E191	2.0	..	0.012	2.0	89	..	2	950	510	49

\*Samples prepared in emulsion (33%) with 0.75% Tergitol Penetrant #4 emulsifying agent; vulcanization recipe; copolymer, 100 parts; 2-mercapto benzothiazole, 0.6-part; zinc oxide, 5 parts; stearic acid, 2 parts; sulfur, 2 parts; tetramethylthiuram disulfide, 1 part; and SRF carbon black, 30 parts.

†Calculated as  $\frac{c}{100}$ .

‡Succinic acid peroxide, 0.033%.

TABLE 9. EMULSION POLYMERIZATION OF MISCELLANEOUS DIENE-ETHYL ACRYLATE MIXTURES

Expt. No.	Diene	Acrylonitrile	Dodecyl Mercaptan	Ammonium Persulfate	Tergitol Penetrant #4	Solids	Temp. °C.	Time, Hours	Yield, %
D58	Cyclopentadiene	2.1	6.0	0.04	0.75	25	82-92	1.7	94
D74	Myrcene	2.1	..	0.08	0.75	25	82-92	0.8	89
D75	Myrcene	2.1	6.0	0.08	0.75	25	82-92	1.0	88
D76	Myrcene	2.1	6.0	0.08	0.75	25	82-92	1.0	89
D78	All-ocimene	2.1	..	1.18	0.75	25	82-92	Did not polymerize	
D89	Divinyl benzene	4.0	..	0.03	0.75	25	79-91	1.7	95
D90	Divinyl benzene	4.0	6.0	0.03	0.75	25	70-91	3.5	92
D91	Divinyl benzene	4.0	6.0	0.03	0.75	25	78-92	2.5	93
D88	2-Methylpentadiene	2.5	6.0	0.77	0.75	25	82-92	8.5	Polymer very soft
E27	2-Chlorobutadiene	5.0	..	0.79	0.50	36	80-91	7.5	96
E48	Vinylcyclohexene	3.3	6.0	0.07	0.45	43	80-90	2	96
E190†	Piperylene	10.0	..	0.24	0.75	33	71-91	5.2	87.5

\*Moisture-free basis.

†1% Triton 720 (moisture-free basis) also used.

TABLE 10. VULCANIZATION\* OF MISCELLANEOUS COPOLYMERS (Preparations Described in Table 9)

Copolymer No.	Curing Time at 298° F. Min.	Tensile Strength P.S.I.	Ultimate Elongation %	Shore A Hardness	Brittle Point °C.
D58	180	490	1540	45	-9
D74	180	430	310	49	-14
D75	60	810	530	52	-6
D76	180	780	460	54	-9
D89	180	210	1080	50	-10
D90	180	920	420	60	-2
D91	180	560	500	60	1
E190	60	830	200	67	...

\*Vulcanization recipe is given in footnote \* of Table 3.

Unsatisfactory (i.e., pitted) products were obtained on attempted vulcanization of copolymers E27 and E48.

**DIMETHYLBUTADIENE-COPOLYMERS.** Although most of the dimethylbutadiene copolymers (Table 8) had moderately high tensile strengths and elongations, the outstanding characteristics of these copolymers were their solubility in organic solvents and the comparative ease with which these materials could be milled. Probably decreased

cross-linkage was an important factor in this behavior. The viscosities of solutions containing 0.05-gram of copolymer in 100 millimeters of toluene indicated that the molecular weights of the copolymers were less than those of some of the ethyl polyacrylate and the chloropropyl acrylate copolymer samples described previously (4).

**MISCELLANEOUS DIENE COPOLYMERS.** The other diene copolymers studied were less satisfactory than the butadiene, isoprene, piperylene and dimethylbutadiene copolymers discussed above. Cyclopentadiene, myrcene, and divinylbenzene (Table 9) apparently yielded vulcanizable copolymers, but the tensile strengths of their vulcanizates were low (Table 10).

Copolymerization occurred with difficulty or not at all when allo-ocimene and methylpentadiene were used. Chloroprene and vinylcyclohexene gave products that could not be molded satisfactorily into test specimens because of pitting or excessive tackiness.

TABLE 11. EMULSION POLYMERIZATION OF ETHYL ACRYLATE AND POLYUNSATURATED ESTERS

		%							Time, Hours	Yield, %
Expt. No.	Polyunsaturated Monomer	Acrylonitrile	Dodecyl Mercaptan	Ammonium Persulfate	Tergitol Penetrant, #4*	Solids				
A259†	Crotyl acrylate	6.4	5	...	...	45			0.7	...
D38	Crotyl acrylate	4.0	...	0.005	0.5	25			1.7	85
D84	Crotyl acrylate	4.0	6	0.055	0.75	25			4.5	57
D85	Crotyl acrylate	4.0	6	0.1	0.055	0.75	25		4.5	91
D35	Cinnamyl acrylate	9.6	...	0.66	0.75	25			2.3	92
D36	Citronellyl acrylate	10.7	...	0.023	0.5	25			1.0	89
D37	Citronellyl acrylate	10.7	6	0.025	0.5	25			3.7	84
D40	Geranyl acrylate	3.2	...	0.01	0.5	25			2.5	82
D63	Geranyl acrylate	3.2	6	0.03	0.75	25			2.0	85
D64	Geranyl acrylate	3.2	6	0.1	0.03	0.75	25		2.0	84
D41	Furfuryl acrylate	2.4	...	0.03	0.50	25			2.0	79
D42	Allyl lactate maleate	5.2	...	0.005	0.50	25			0.7	56
D43	Allyl lactate maleate	5.2	...	0.01	0.50	25			0.7	72
D61	Diethylene glycol bis-(allyl carbonate)	7.5	...	...	0.50	25			0.7	91
D62	Diethylene glycol bis-(allyl carbonate)	7.5	6	...	0.50	25			1.2	93
D65	Rhodinyl acrylate	6.5	...	0.05	0.75	25			2.0	97
D66	Rhodinyl acrylate	6.5	6	0.05	0.75	25			2.5	84
D67	Rhodinyl acrylate	6.5	6	0.1	0.03	0.75	25		1.8	83
E204‡	Allyl phthalate	5.0	...	...	0.38	33			0.8	...
D86	Allyl maleate	3.0	3	0.1	0.0003	0.50	40		7.0	75
E10	Allyl maleate	0.1	...	0.022	0.50	32			1.2	94
D101	Methyl pentenyl acrylate	4.8	...	0.053	0.67	33			3.0	84
D101	Methyl pentenyl acrylate	4.8	6	0.053	0.67	33			2.5	91
D102§	Methyl pentenyl acrylate	4.8	6	0.1	0.053	0.67	33		1.8	93

\*Calculated as 25% emulsifying agent.

†Triton K60, 0.5; and 0.5% of 30% hydrogen peroxide used.

‡Triton 720, 1% (calculated as 30% solids).

§Intrinsic viscosity of polymer, 2.14.

TABLE 12. VULCANIZATION\* OF ETHYL ACRYLATE AND POLYOLEFINIC ESTER COPOLYMERS

(Preparation Described in Table 11)

Copolymer No.	Curing Time at 298° F., Hours	Tensile Strength P.S.I.	Ultimate Elongation %	Shore A Hardness	Brittle Point °C.
A259	0.5	1470	310	64	-1
D38	3	1110	300	54	-14
D84	3	1200	350	60	-5
D85	3	1220	340	59	-14.5
D36	3	740	210	53	-10
D37	3	1000	230	52	-19
D40	3	1110	300	58	-7
D63	3	1310	340	58	-10
D64	1	1380	370	48	-15
D41	3	310	850	49	-18
D42	3	540	230	54	-14
D65	1	580	160	54	-8
D66	2	1090	220	62	-7
D67	2	1100	220	58	...
E204†	3	190	460	33	...
D86†	4	140	1070	45	...
E10†	2	1470	640	50	...
D101†	2	0	50	75	...
D102†	2	0	60	75	...

\*Vulcanization recipe is given in footnote \* of Table 3.

†Stock did not vulcanize.

‡Recipe: Copolymer, 100 parts; red lead, 10 parts; zinc oxide, 10 parts; stearic acid, 3 parts; p-quinone dioxime, 2 parts; and SRF carbon black, 30 parts.

## Ester Copolymers

Copolymers of ethyl acrylate and allyl maleate had been studied previously (2), but methods for preparing rubbery products having high tensile strength had not been found. Since dodecyl mercaptan and acrylonitrile were beneficial in the earlier preparation of allyl maleate co-

polymers, these two materials were used in some experiments of the present study (Table 11).

Unlike the diene copolymerizations discussed above, in general the copolymerization of the polyolefinic esters with ethyl acrylate followed a more normal course with respect to the amount of catalyst and time of polymerization. The higher boiling points of the polyolefinic esters permitted the use of uniformly higher initial refluxing temperatures and minimized loss during the polymerization.

The crotyl and geranyl acrylate (12) copolymers yielded the best vulcanizates (Table 12, D63, D64, D84, and D85). Although the tensile strengths of their vulcanizates were moderately high, the ultimate elongation was always less than 400%. Crotyl acrylate was found in an earlier study (12) to have relatively little tendency to form cross-linked copolymers when polymerized with methyl acrylate in an ethyl acetate solution. Geranyl acrylate, however, readily formed cross-linked copolymers with methyl acrylate (12). The cinnamyl acrylate and furfuryl acrylate copolymers were inelastic. The diethylene glycol bis-(allyl carbonate) (24, 25) copolymer vulcanizates were not suitable for testing.

## Ethyl Acrylate-Ether Copolymers

The only unsaturated ether copolymer that yielded a satisfactory vulcanizate was that obtained from vinyl ether (Table 13). The vinyl ether copolymer of Expt.

TABLE 13. EMULSION POLYMERIZATION AND VULCANIZATION OF ETHYL ACRYLATE AND POLYOLEFINIC ETHER COPOLYMERS

		%							Time, Hours	Yield %	Curing Time at 298° F. Hours	Tensile Strength %	Ultimate Elonga- %	Shore A Hardness	Brittle Point °C.
Expt. No.	Polyolefinic Ether	Acrylo- nitrile	Dodecyl Mercaptan	Ammonium Persulfate	Tergitol Penetrant #4†	Solids									
D55	Vinyl ether	2.1	..	0.01	0.75	25	0.5	96	3	380	950	41	-19		
D6	Vinyl ether	2.1	6	0.03	0.75	25	0.7	93	3	1280	960	48	-12		
D557	Vinyl ether	2.1	6	0.1	0.02	0.75	25	1.0	94	3	910	1280	47	-10	
D68	Allyl ether‡	3.0	..	0.03	0.75	25	1.3	88	1	<100	>2400	36	..		
D69	Allyl ether‡	3.0	6	0.03	0.75	25	1.8	89	2	<100	>2200	45	..		
D103	Methallyl ether‡	4.0	..	0.02	0.67	38	0.8	91.5	2	<100	100	60	..		
D104	Methallyl ether‡	4.0	6	0.074	0.67	38	2.8	93	2	<100	100	65	..		
D105	Methallyl ether‡	4.0	6	0.13	0.67	38	1.0	79	2	<100	100	68	..		
D77	Allyl methyl glucoside‡§	4.2	..	0.03	0.75	25	0.5	95	3	140	120	59	..		
E16	Diallyl glycol‡	2.4	..	0.06	1.25	20	1.0	92	4	100	510	42	..		
E17	Diallyl glycol	3.0	6	0.08	1.25	20	1	87	2	510	580	45	..		

\*Vulcanization recipe is given in footnote \* of Table 3.

†Moisture-free basis.

‡Stock did not vulcanize.

§Approximately 3.5 allyl groups.